

## COMETS: A LINK BETWEEN INTERSTELLAR AND NEBULAR CHEMISTRY

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The chemical and isotopic composition of comets is reviewed, with emphasis on results obtained since the *Protostars and Planets III* conference. Observations from the apparitions of comets Hyakutake (C/1996 B2) and Hale-Bopp (C/1995 O1) have almost tripled the number of known cometary parent molecules, including nonpolar hydrocarbons observed in the infrared. Large D/H fractionation has been observed for water and HCN, whereas the carbon, nitrogen, and sulfur isotopic ratios appear to be solar. Cometary dust has been shown to include both crystalline and amorphous silicates, including both olivines and pyroxenes. The dust thus appears similar to that observed in some interplanetary dust particles (IDPs) and to some circumstellar grains. The chemistry of potential cometary volatiles in the solar nebula is reviewed and is contrasted with that expected for preserved interstellar matter. We conclude that cometary nuclei likely contain interstellar material that has been partially processed in the nebula and partially diluted with nebular condensates. The chapter concludes with recommendations for future observational, laboratory, and theoretical work that could clarify the origin of cometary matter.

### I. INTRODUCTION

The structure and chemical composition of comets clearly provide key data on the processes and conditions in the outer solar system at the time of its formation and potentially in the interstellar molecular cloud from which the solar nebula condensed (the “natal cloud”). Cometary nuclei are the most volatile-rich, and hence the least thermally processed, material that

enters the inner solar system. This does not mean that comets are pristine samples of the ancient solar system. Numerous processes over the last 4.5 Gyr can affect their nature: cosmic rays; the interstellar radiation field; heating pulses from passing stars and from supernovae while the nuclei are in the Oort Cloud or Edgeworth-Kuiper Belt; and, of course, solar irradiation as the comets approach the Sun. Nonetheless, the record that comets preserve should be substantially easier to read than that in the planets, satellites, asteroids, and meteorites, which have been chemically differentiated or at least volatile depleted relative to the nebula as a whole.

Of crucial importance to many issues concerning the formation of solar-type stars and planetary systems is the question of whether or not comets contain relatively unprocessed interstellar molecular material. In the classical view of planetesimal formation, the solar nebula began in a sufficiently hot state that any preexisting matter was vaporized to its atomic constituents and was well mixed. Subsequently, as the nebula cooled, solids condensed in accordance with thermochemical equilibrium, resulting in a gradient in composition with respect to distance from the Sun that reflected the corresponding temperature and density gradients (Lewis 1972). In the outer portions of the nebula the cold temperature led to efficient condensation of volatiles, producing the nuclei of the comets (and other icy objects). However, as noted long ago by Urey (1953), "at lower temperatures [in the solar nebula] thermodynamic equilibrium may not be reached even in periods of time that are long compared to the age of the universe, and at these temperatures the kinetics of thermal reactions or of photochemical reactions become important." Lewis and Prinn (1980) subsequently showed that the conversion of the dominant high-temperature equilibrium species, CO and N<sub>2</sub>, to methane and ammonia is so slow that only minor amounts of NH<sub>3</sub> and CH<sub>4</sub> should be present in the solar nebula itself. However, in the higher-density subnebulae around the forming jovian planets, these conversions can proceed rapidly, so CH<sub>4</sub> and NH<sub>3</sub> are expected to be the dominant carbon- and nitrogen-bearing gases in those environments (Prinn and Fegley 1981, 1989).

In contrast, Greenberg (1982, 1998) has long argued that comets are fundamentally aggregates of ice-mantled interstellar grains that survived the formation of the nebula. If this view is correct, it has profound implications for the character of the processes by which matter accreted into the outer nebula, requiring that passage through any accretion shock be a rather gentle process. Moreover, it would mean that comets were direct probes of the nature of the natal cloud and of the interstellar medium (ISM) in a more general sense. It is now generally accepted that meteorites contain refractory presolar grains such as SiC, diamond, graphite, and Si<sub>3</sub>N<sub>4</sub> (Zinner 1997), and isotopic data also strongly suggest that organic material in carbonaceous chondrites contains interstellar molecules or their immediate derivatives (Cronin and Chang 1993; Cronin et al. 1995; Messenger

and Walker 1997). If the latter view is indeed correct, then it would seem hard to avoid the conclusion that even more interstellar material is preserved in comets. The striking similarities in the composition of cometary and interstellar ices point in this direction, as will be discussed in this review, but the alternative possibility (that such similarities simply reflect general properties of low-temperature, disequilibrium chemistry in solar-composition material) must be borne in mind.

Since there have been as yet no *in situ* analyses of cometary nuclei, and only one set of close spacecraft encounters with a comet (Halley), deducing the nature of comets remains a matter of interpreting the complex and interlinked physics and chemistry of the processes that produce the coma and tail as the nucleus approaches the Sun. Much progress has been made in recent years as advances in instrumentation have allowed the detection of "parent" molecules, which presumably have sublimated from the nucleus, in addition to their photodissociation and photoionization products ("daughter" molecules) traditionally observed at optical and ultraviolet wavelengths. However, many questions remain concerning chemistry in the coma, fractionation during the complex sublimation process, release of molecules from solid grains, and other processes that influence the interpretation of coma observations. Some of these will be discussed below. It remains clear, however, that space missions that actually sample cometary nuclear material are extremely important.

The period since *Protostars and Planets III* has produced extremely important results for our understanding of comets. In part this has been due to the fortuitous apparitions of two very bright comets: C/1996 B2 (Hyakutake), a moderately active comet that passed very close to the Earth, and C/1995 O1 (Hale-Bopp), a very active comet. The impact of D/1993 F2 (Shoemaker-Levy 9) with Jupiter provided a unique opportunity to study the internal strength of a comet as well as other phenomena associated with this encounter (Noll et al. 1996). These and other observations were facilitated by new astronomical instrumentation, including spacecraft, and have resulted in major discoveries in the composition and nature of comets. Among these results has been the discovery of a whole new set of solar system objects in the Kuiper Belt that are certainly related to comets (see chapters by Jewitt and Luu, Farinella et al., and Malhotra et al., this volume), as well as the unexpected detection of X-ray emission from comets, which, however, is probably more related to the solar wind or to the solar UV spectrum than to the nature of comets themselves (e.g., Lisse et al. 1996, 1998; Mumma et al. 1997*b*; Dennerl et al. 1997; Cravens 1997; Krasnopolsky 1997; Krasnopolsky et al. 1997).

Although no single review can cover all aspects of comets, that at *Protostars and Planets III* by Mumma et al. (1993) was very comprehensive. Consequently, the present paper will focus on recent results rather than seeking great breadth. We do point out the following other recent

reviews concerning comets: A'Hearn (1998), A'Hearn et al. (1998), Eberhardt (1999), Campins (1998), Sekanina et al. (1998), and the references that begin section III.A.

## II. INTERSTELLAR GRAINS

In considering the question of whether comets consist of or contain interstellar molecular material, it is obviously crucial to investigate the nature of interstellar solids. The latter include quite refractory material such as silicates and silicon carbide, both refractory and more volatile organic matter, and ices. There has been significant progress toward understanding the nature of interstellar grains in the last several years, in part because of the success of the *Infrared Space Observatory* (ISO), but very fundamental questions remain.

Direct investigation of the interstellar grains can be carried out by infrared spectroscopy as well as by the traditional studies of the interstellar extinction and polarization in the ultraviolet, visible, and near infrared. In addition, it remains possible that some of the Diffuse Interstellar Bands (DIBs) may originate in the grains, and DIBs as well as other phenomena strongly suggest the presence of interstellar polycyclic aromatic hydrocarbon molecules (PAHs), which may simply be the small end of a continuous spectrum of grain sizes (e.g., Salama 1996; Snow 1997). Moreover, because there is certainly interchange of material between the gas and solid phases in dense interstellar clouds, the composition of the gas provides clues to that of the grains in various environments; this is very important, because the gas can be observed at high spectral resolution and sensitivity at millimeter and submillimeter wavelengths.

The precise nature of the bulk of the organic matter in interstellar grains remains unknown, however (cf. Tielens et al. 1996). This is perhaps not surprising, given the difficulty in characterizing the organic matter in the comet Halley CHON particles (e.g., Fomenkova 1997), in the matrix of carbonaceous chondrites (Cronin and Chang 1993), and in terrestrial kerogens, in spite of the analytical tools that can be brought to bear on these samples. The apparent preservation of interstellar organic molecules in carbonaceous chondrites and the mass spectroscopy of the CHON particles suggest, however, that comets contain complex, heteropolymeric organic matter, some of which may include the corresponding portion of interstellar grains.

Knowledge of interstellar and circumstellar silicates has grown significantly over the last few years with the ability of ISO to obtain complete infrared spectra over the range  $2.4 \leq \lambda \leq 45 \mu\text{m}$  (and, at lower resolution,  $43 \leq \lambda \leq 196 \mu\text{m}$ ). Circumstellar silicates are seen to include both amorphous and crystalline material, including both olivines  $[(\text{Mg,Fe})_2\text{SiO}_4]$  and pyroxenes  $[(\text{Mg,Fe,Ca})\text{SiO}_3]$  (Waelkens et al. 1998;

Malfait et al. 1998). Curiously, in the interstellar environment (away from circumstellar envelopes and disks), crystalline silicates have not been identified. The greater similarity of the Hale-Bopp silicates to those in circumstellar as opposed to interstellar environments is puzzling (see section III.B).

The volatile content of comets provides the most stringent constraints on their origin, so the comparison with interstellar ices is particularly interesting. Here two sources of new data are especially important: (i) ISO and ground-based spectra of icy grain mantles in molecular clouds and (ii) millimeter/submillimeter observations of gas-phase molecules in “hot cores”: regions of high-mass star formation in molecular clouds where the grain mantles have been sublimated and/or sputtered from grains. These topics are reviewed in van Dishoeck and Blake (1998) and in the chapter by Langer et al., this volume. A definite similarity exists between interstellar ices and comets in both chemical composition and deuterium/hydrogen fractionation. However, several limitations in such comparisons should be borne in mind.

1. The sensitivity of the infrared spectra limits the identifiable ice constituents to those with abundances  $\geq 0.5\%$  relative to the principal component,  $\text{H}_2\text{O}$ .
2. The gas in hot cores includes the products of prestellar, cold, predominantly ion-molecule chemistry; molecules synthesized on the grains and subsequently released to the gas phase; and products of further chemical processing of the first two components in the gas heated by the young stars. Distinguishing among these components is not easy (e.g., it is unclear whether ethanol is synthesized on the grains or by high-temperature gas-phase reactions; Millar and Hatchell 1998), so the deduced composition of the icy grain mantles is model dependent.
3. Moreover, the hot core environment itself, representing a region of high-mass star formation, differs in unclear ways from that in regions of low-mass star formation, which may be more similar to that in which the solar nebula formed.

Isotopic abundances provide a particularly useful probe of chemical processes. The large deviations from terrestrial isotopic ratios for several elements in portions of meteoritic material provide the principal argument for the preservation of interstellar matter in these objects (e.g., Cronin and Chang 1993; Cronin et al. 1995). In comparing differences in isotopic ratios between the interstellar medium and comets, it is important to differentiate between overall nuclear isotope abundances (e.g.,  $^{12}\text{C}/^{13}\text{C}$ ), which are the result of ongoing nucleosynthesis in stars and typically show gradients with respect to both galactocentric distance and time, and chemical fractionation, which concentrates a particular isotope in specific molecular species under certain physical conditions. The Sun formed about 4.5 Gyr ago and, it is now believed, about 2 kiloparsecs closer to the

center of the Galaxy than its current location (Wielen et al. 1996), so the most relevant comparisons for solar system objects are with conditions at that position at that time, not with the local ISM today. Although there is considerable scatter in the data, perhaps as a result of local star formation history, the trends vs. galactocentric distance agree with current models for the relative abundances of the isotopes of C, N, and O (cf. Wielen and Wilson 1997, and references therein); the observed gradients for sulfur isotopes may require modifications to current theories (Chin et al. 1996). Estimates of the temporal evolution, in contrast, are based primarily on comparisons with current solar system values for all these elements.

Superimposed on these general trends of galactic isotopic evolution are chemical fractionation among and within clouds, due to variations in factors such as the UV field, electron density, kinetic temperature, overall density, and stochastic fluctuations such as might result from recent nearby supernovae. The very large D/H fractionation observed for many interstellar molecular species (up to 4 orders of magnitude) is reasonably well understood to be the result of both gas-phase and grain surface processes at low temperatures (e.g., Rodgers and Millar 1996; Irvine and Knacke 1989; Tielens 1983). The effects are much smaller for heavier atoms, but carbon isotope fractionation (up to a factor of a few) in particular sources (e.g., Langer et al. 1984; Taylor and Dickman 1989), and even differential  $^{13}\text{C}/^{12}\text{C}$  fractionation among the carbons at different positions in  $\text{HC}_3\text{N}$  in a given cloud (Takano et al. 1998), are observed. Chemical fractionation of oxygen is not thought to be significant under most conditions in the ISM (Langer et al. 1984); in addition, it would be difficult to separate from carbon isotopic fractionation, because the principal observed gas-phase reservoir for both C and O is CO. Although some fractionation might in principle occur at very low temperatures for nitrogen, the large  $^{14}\text{N}/^{15}\text{N}$  ratio would make it very difficult to measure (Guélin and Lequeux 1980). Fractionation is also expected to be small for sulfur, although there are some theoretical and observational suggestions that cold, dark clouds may be enhanced in  $^{34}\text{S}$  relative to  $^{32}\text{S}$  (Chin et al. 1996; Pratap et al. 1997) compared to warmer sources, perhaps by of order 40%. Comparisons to isotope ratios observed in comets are described below. It is unfortunate that the difficulty in observing through the terrestrial atmosphere has thus far precluded measurement of the  $\text{HDO}/\text{H}_2\text{O}$  fractionation in regions of low-mass star formation.

Likewise, the interesting results on the ortho-to-para abundance ratio for water in several recent comets (see below) cannot yet be compared to interstellar values, although such ratios have been measured for other molecular species in cold interstellar clouds (e.g.,  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{CCO}$ ,  $\text{H}_2\text{CS}$ ,  $\text{C}_3\text{H}_2$ ; Irvine 1992; Minh et al. 1995). Interestingly, a difference in the ratio for formaldehyde may exist between cold cloud cores with and without embedded young low-mass stars (Dickens 1998).

### III. THE COMPOSITION OF COMETS

#### A. The Composition of Cometary Volatiles

The composition of comets, as it was known at the time of the previous *Protostars and Planets* conference, was reviewed by Mumma et al. (1993), Festou et al. (1993), and Crovisier (1994). More recent results, including those from comets Hyakutake and Hale-Bopp, are described by Bockelée-Morvan (1997), Mumma (1997), Eberhardt (1998), Rauer (1999), and Bockelée-Morvan and Crovisier (1998); see also Crovisier (1998*a,b*; 1999) and Despois (1998). The improvement coming from the observations of these last two comets is really significant, because it increased the number of known *parent* molecules from about 8 to about 22. Our present knowledge of the composition of cometary volatiles is summarized in Table I. A sample spectrum is shown in Fig. 1.

Most of these new molecules have been detected through their rotational lines at radio wavelengths. This technique is very sensitive even to minor species, provided they are polar molecules. In addition to the previously known HCN, important new cyanide-containing molecules have been identified: HNC, an isomeric form of HCN (Irvine et al. 1996; see discussion in section V.B); and CH<sub>3</sub>CN and HC<sub>3</sub>N, pointing to the possible existence of carbon chain molecules such as those found in interstellar clouds (Bockelée-Morvan et al. 1998*b*). Ammonia has been firmly identified for the first time through its centimetric lines (Bird et al. 1997; Palmer et al. 1996).

Several new sulfur-bearing molecules have been identified to complement the already known H<sub>2</sub>S and CS<sub>2</sub> (the probable parent of CS). Surprisingly, SO and SO<sub>2</sub> were observed with a significant abundance, much higher than the upper limits previously inferred from UV data (Kim and A'Hearn 1991), which indicates that the UV excitation of these molecules has perhaps not been understood (Bockelée-Morvan et al. 1998*b*; Lis et al. 1998). OCS and H<sub>2</sub>CS were observed for the first time as minor constituents (Woodney et al. 1997, 1998; Dello Russo et al. 1998*a*). The mysterious S<sub>2</sub>, previously observed only in C/1983 H1 (IRAS-Araki-Alcock), was observed again in the near UV in comet Hyakutake (Weaver et al. 1996), the detection of this short-lived molecule benefiting in these two cases from the close approach of the comet to the Earth. Interferometric observations of Hale-Bopp suggest that SO may be in part a daughter radical produced from SO<sub>2</sub> photolysis in the coma (Wink et al. 1998).

Several CHON (organic) species have been detected with minor abundances relative to the previously known methanol and formaldehyde: formic acid (HCOOH), isocyanic acid (HNCO), methyl formate (HCOOCH<sub>3</sub>), and formamide (NH<sub>2</sub>CHO); see Bockelée-Morvan et al. (1998*b*) and Lis et al. (1997, 1998). In addition, significant upper

**TABLE I**  
Abundances of Cometary Volatiles

Molecule	Abundance <sup>a</sup>		Method <sup>b</sup>	N <sup>c</sup>	Comments
	Hale-Bopp	Other Comets			
H <sub>2</sub> O	= 100	= 100	IR	6	Also indirect (from OH, O, H)
CO	20	1–20	UV, radio, IR	>5	Extended source?
CO <sub>2</sub>	20 <sup>d</sup>	3–10	IR	3	
H <sub>2</sub> CO	0.1–1	0.1–1	Radio, IR	>5	Extended source
CH <sub>3</sub> OH	2	1–7	Radio, IR	>5	
HCOOH	~0.05		Radio	1	
HNCO	0.1		Radio	2	
NH <sub>2</sub> CHO	~0.01		Radio	1	
HCOOCH <sub>3</sub>	~0.05		Radio	1	
CH <sub>4</sub>	~0.6		IR	2	
C <sub>2</sub> H <sub>2</sub>	~0.1		IR	2	
C <sub>2</sub> H <sub>6</sub>	~0.3		IR	2	
NH <sub>3</sub>	0.6		Radio, IR	3	
HCN	0.2	0.05–0.2	Radio, IR	>5	
HNC	0.04		Radio	2	Extended source?
CH <sub>3</sub> CN	0.02		Radio	2	
HC <sub>3</sub> N	0.03		Radio	1	
H <sub>2</sub> S	1.5	0.2–1.5	Radio	>5	
H <sub>2</sub> CS	~0.02		Radio	1	
CS	0.2	0.2	UV, radio	>5	From CS <sub>2</sub> ?
OCS	0.5		Radio, IR	2	Extended source?
SO	~0.5		Radio	1	From SO <sub>2</sub> ?
SO <sub>2</sub>	~0.1		Radio	1	
S <sub>2</sub>		0.005	UV	2	

<sup>a</sup> Abundance relative to water. See text for references. All abundances were measured at  $r_h \sim 1$  AU except for CO<sub>2</sub> in Hale-Bopp. Listed abundances may be uncertain by a factor of 2 or more for some species and may not pertain to nucleus production for “extended sources.”

<sup>b</sup> Method of observation.

<sup>c</sup> Number of comets in which this species was reliably and directly observed.

<sup>d</sup> Measured at  $r_h = 2.9$  AU.



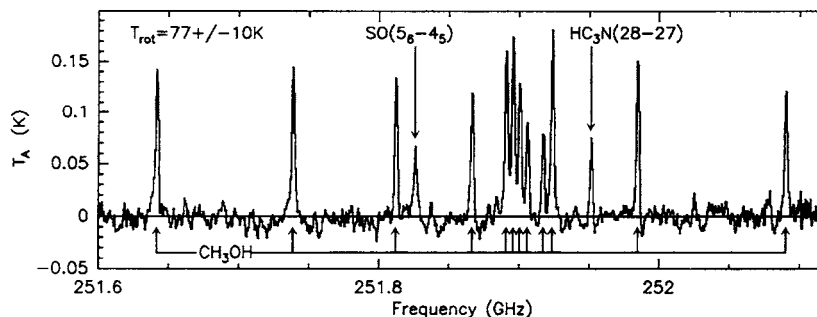


Figure 1. A spectrum of comet Hale-Bopp observed at the Caltech Submillimeter Observatory (CSO) on February 21, 1997, showing a series of lines of methanol and the corresponding rotational temperature, and the first observations of SO and HC<sub>3</sub>N in a comet (Lis et al. 1998). Such data illustrate the power of millimeter and submillimeter-wavelength observations for cometary studies.

limits have been obtained for molecules such as methylenimine (CH<sub>2</sub>NH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), ketene (CH<sub>2</sub>CO), and many others.

The infrared is a unique domain for observing nonpolar species that do not have allowed rotational transitions as well as for obtaining new information on molecules also observed at radio wavelengths. Identifications of hydrocarbons in comets Hyakutake and Hale-Bopp from new ground-based observations (Mumma et al. 1996; Brooke et al. 1996; Weaver et al. 1998) include C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub> (Fig. 2). Numerous other parent volatiles were detected at infrared wavelengths (e.g., CO, CH<sub>3</sub>OH, HCN, H<sub>2</sub>CO, OCS, NH<sub>3</sub>), and sensitive searches were performed for other species (e.g., C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, O<sub>3</sub>), although actual upper limits are not yet available.

Water has been detected from ground-based observatories only at infrared wavelengths. The approach of hot-band fluorescence developed for earlier comets was applied to comet Hyakutake (Mumma et al. 1996) and for Hale-Bopp was used to obtain production rates for various heliocentric distances (Dello Russo et al. 1999; Weaver et al. 1998). Observations of water in Hale-Bopp and 103P/Hartley 2 from space (with ISO) provided production rates and the ortho-para ratio, which agree well with those obtained for 1P/Halley (see section III.D).

The high spatial resolution afforded by long-slit spectrometers permits detailed study of the distribution of molecular emissions about the nucleus. These can discriminate nuclear from extended sources of "parent" volatiles. CO was studied in this way; similarly to comet 1P/Halley, when comet Hale-Bopp was at a heliocentric distance of approximately 1 AU, up to 50% of the CO was found to be produced from an extended source (DiSanti et al. 1999; Weaver et al. 1998). Water and HCN,

## C/1996 B2 Hyakutake, UT March 24.5, 1996

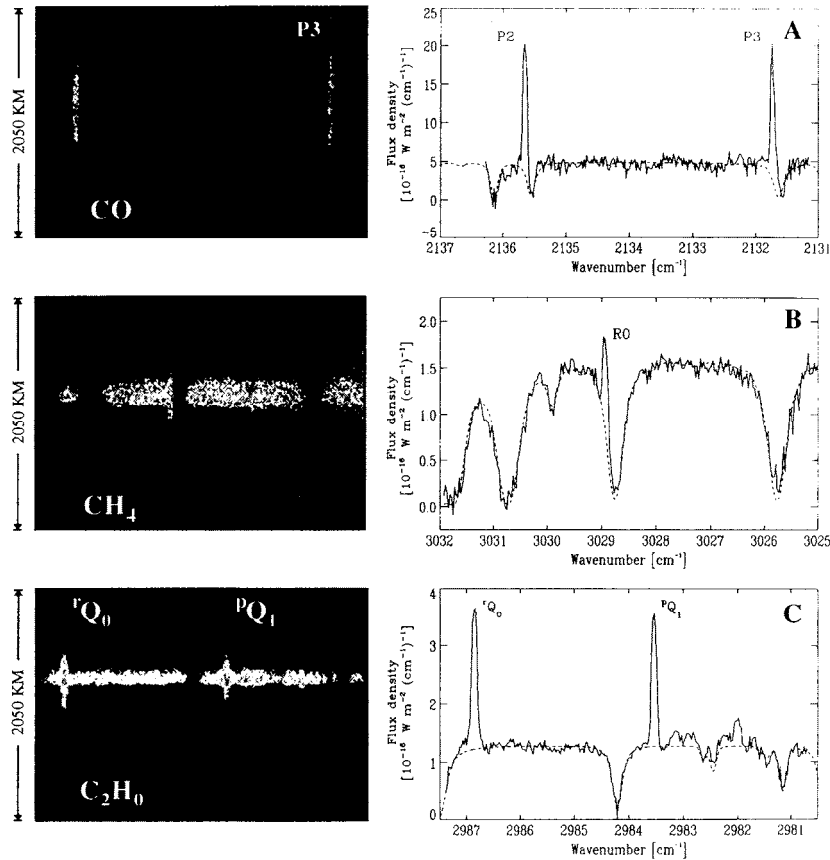


Figure 2. High-dispersion ( $R = 20,000$ ), long-slit spectra ( $0.2$  arcsec per pixel) of comet Hyakutake, showing emission from parent volatiles and dust. Full spectral-spatial frames are shown at left, and corresponding spectra extracted for seven rows centered on the nucleus are shown at right. Telluric lines are seen in absorption against the cometary continuum, and their cometary counterparts are Doppler-shifted to higher frequencies by the comet's motion. (*top*) The P2 and P3 lines of the carbon monoxide 1–0 vibrational band near  $4.69 \mu\text{m}$ ; (*middle*) the R0 line of the methane  $\nu_3$  band near  $3.30 \mu\text{m}$ ; (*bottom*) The  $\text{P}'\text{Q}_0$  and  $\text{P}'\text{Q}_1$  branches of the ethane  $\nu_7$  band near  $3.351 \mu\text{m}$ . These are the discovery spectra for saturated hydrocarbons in comets (Mumma et al. 1996).

however, appear to be released directly from the nucleus (Dello Russo et al. 1999, Magee-Sauer et al. 1998; Weaver et al. 1998). A comparison of the spatial distribution for OCS relative to those of water and dust in Hale-Bopp provided evidence that most OCS was produced from an extended source (Dello Russo et al. 1998a). The rotational temperature measured

for CO and HCN in Hale-Bopp revealed changes in the coma temperature with distance from the nucleus, similar to those predicted by models of photolytic heating (DiSanti et al. 1999; Magee-Sauer et al. 1998; Bockelée-Morvan and Crovisier 1987). The ability to distinguish direct and extended sources for “parent” volatiles is key to understanding the composition of cometary ices.

The ISO provided the second direct observation of CO<sub>2</sub> in a comet (Crovisier et al. 1996, 1997*b*) through its  $\nu_3$  band at 4.25  $\mu\text{m}$ . CO<sub>2</sub> can also be traced following its photodissociation from the CO Cameron system in the UV (e.g., Weaver et al. 1997). The direct detection is important; CO<sub>2</sub> production rates cannot be reliably derived from the UV observations because the rates of the relevant mechanisms are still poorly known.

Some words of caution are necessary concerning the relationship between reported “production rates” of cometary volatiles observed in the coma (as listed in Table I) and the actual molecular abundances in cometary ices:

1. *Sublimation fractionation* affects all production rates, depending on the heliocentric distance. This is now clearly shown by the evolution of production rates observed over the range of distance 1–7 AU in comet Hale-Bopp, which show significant variations relative to water for several species (Biver et al. 1997, 1998).
2. *Chemical reactions* in the coma may be able to synthesize some species of minor abundance in highly productive comets where the coma density could be high. This was evident from the [HNC]/[HCN] ratio varying with the heliocentric distance in Hale-Bopp (see the discussion in section V.B). Thus, one might question the significance of the abundances of some of the minor species detected in comet Hale-Bopp near its perihelion.
3. The existence of *extended sources* within the coma has been demonstrated for molecules such as CO, H<sub>2</sub>CO, OCS, and perhaps others. The sources of such molecules are poorly known. They might be grains with CHON mantles, but the desorption mechanism of molecules is still uncertain (see, e.g., Crovisier 1998*a*; Greenberg and Li 1998). For these molecules the production rates may not pertain to sublimation from the nucleus and thus may not be relevant to nuclear ice abundances.

## B. The Composition of Cometary Dust

In addition to the *in situ* analysis of P/Halley’s dust particles by mass spectroscopy (recently reanalyzed by Schulze et al. 1997 and Eberhardt 1999), which revealed the *elemental* rather than the *chemical* composition, the composition of cometary dust can be investigated by spectroscopy in the thermal infrared. Until recently, most of the clues came from the

analysis of the intricate band around 10  $\mu\text{m}$ . It revealed the presence of silicates, part of them being crystalline in some comets (e.g., Hanner et al. 1994).

ISO gave us, for the first time, access to the full infrared spectrum of a comet, from 2.4 to 196  $\mu\text{m}$ , covering thermal emission of cometary dust. In addition to the already well-known silicate bands around 10 and 20  $\mu\text{m}$ , the observations of comet Hale-Bopp revealed peaks at 16, 23.5, 27.5, and 33.5  $\mu\text{m}$  (Crovisier et al. 1997*a,b*). These were identified with Mg-rich olivine (forsterite,  $\text{Mg}_2\text{SiO}_4$ ). The Hale-Bopp spectrum appears strikingly similar to those of circumstellar dust around Vega-type stars (e.g., that of HD 100546, a Herbig Ae star; Waelkens et al. 1996; Malfait et al. 1998). Quantitative fits of the ISO spectra (with still preliminary calibration) with laboratory spectra of terrestrial and IDP (interplanetary dust particles) analogs reveal that, in addition to forsterite, amorphous silicates as well as a featureless component (such as amorphous carbon) are necessary to reproduce the spectra (Hanner et al. 1998; Brucato et al. 1999; Wooden et al. 1999).

ISO could observe comet Hale-Bopp only at heliocentric distances greater than 2.9 AU. In ground-based spectra in the 8–13  $\mu\text{m}$  window, features characteristic of pyroxene (at 9.3 and 10.0  $\mu\text{m}$ ) appeared at smaller heliocentric distances, implying the existence of two crystalline grain components with different temperatures: the hotter including olivines, the cooler, pyroxenes (Wooden et al. 1999). The dust of comet Hale-Bopp, with Mg-rich pyroxenes and olivines, thus seems to have a composition comparable with that of IDPs (Bradley et al. 1988, 1997). This composition is also compatible with that predicted for the first Mg silicates to condense from a solar-composition gas (Grossman and Larimer 1974).

Do Jupiter-family comets, presumed to have formed in the Edgeworth-Kuiper Belt, have the same composition as Oort Cloud comets? The former are fainter and more difficult to observe. Until recently, silicate bands were undetected or gave inconclusive results in the few Jupiter-family comets that were observed (e.g., Hanner et al. 1996). However, observations of 103/P Hartley 2 with ISO have now revealed the 11.3  $\mu\text{m}$  feature characteristic of crystalline olivine (Crovisier et al. 1999).

### C. Isotopic Abundances

Isotopic abundances (and especially the [D]/[H] ratio in water) in comet Halley from the *Giotto* mass spectrometers have now been refined (Balsiger et al. 1995; Eberhardt et al. 1995). In addition, new results were obtained from radio spectroscopic observations of comets Hyakutake and Hale-Bopp, resulting in determinations of the [D]/[H] ratios in water (Bockelée-Morvan et al. 1998*a*; Meier et al. 1998*b*) and HCN (Lis et al. 1998; Meier et al. 1998*a*), and of C, N, and S isotopic ratios in HCN and CS (Jewitt et al. 1997). All these results are summarized in Table II. A

**TABLE II**  
Isotopic Ratios in Comets

Isotopes	Molecule	Comet	Method	Cosmic Value	Comet Value	Reference
[D]/[H]	H <sub>3</sub> O <sup>+</sup>	Halley	Mass spect.	$1.5 \times 10^{-5}$	$3.08 \pm 0.53 \times 10^{-4}$	Balsiger et al. (1995)
	H <sub>2</sub> O	Hyakutake	Radio		$3.02 \pm 0.22 \times 10^{-4}$	Eberhardt et al. (1995)
		Hale-Bopp	Radio		$2.9 \pm 1.0 \times 10^{-4}$	Bockelée-Morvan et al. 1998a
	HCN	Hale-Bopp	Radio		$3.3 \pm 0.8 \times 10^{-4}$	Meier et al. (1998b)
	CH <sub>3</sub> OH <sup>a</sup>	Halley	Mass spect.		$2.3 \pm 0.4 \times 10^{-3}$	Meier et al. (1998a)
[ <sup>18</sup> O]/[ <sup>16</sup> O]	H <sub>3</sub> O <sup>+</sup>	Halley	Mass spect.	$2.0 \times 10^{-3}$	$< 1 \times 10^{-2}$	Eberhardt et al. (1994)
					$1.93 \pm 0.12 \times 10^{-3}$	Balsiger et al. (1995)
					$2.13 \pm 0.18 \times 10^{-3}$	Eberhardt et al. (1995)
[ <sup>13</sup> C]/[ <sup>12</sup> C]	CN	Halley	Visible	$1.1 \times 10^{-2}$	$1.05 \pm 0.13 \times 10^{-2}$	Kleine et al. (1995)
	HCN	Hyakutake	Radio		$2.9 \pm 1.0 \times 10^{-2}$	Lis et al. (1997)
		Hale-Bopp	Radio		$1.11 \pm 0.18 \times 10^{-2}$	Lis et al. (1998)
					$0.90 \pm 0.09 \times 10^{-2}$	Jewitt et al (1997)
[ <sup>15</sup> N]/[ <sup>14</sup> N]	CN	Halley	Visible	$3.6 \times 10^{-3}$	$< 3.6 \times 10^{-3}$	Kleine et al. (1995)
	HCN	Hale-Bopp	Radio		$3.1 \pm 0.4 \times 10^{-3}$	Jewitt et al. (1997)
[ <sup>34</sup> S]/[ <sup>32</sup> S]	Atomic S	Halley	Mass spect.	$4.2 \times 10^{-2}$	$4.5 \pm 1.0 \times 10^{-2}$	Krankowsky et al. (1986)
	CS	Hale-Bopp	Radio		$3.7 \pm 0.4 \times 10^{-2}$	Jewitt et al. (1997)

<sup>a</sup> [CH<sub>3</sub>OD + CDH<sub>2</sub>OH]/[CH<sub>3</sub>OH].

detailed discussion of the significance of the [D]/[H] ratio in comets is given in section IV.A below; cf. also Mumma (1997) and Bockelée-Morvan et al. (1998a).

The mean C, N, and S isotopic ratios are not significantly different from the solar values. This confirms, with an improved accuracy, previous determinations for volatiles from optical spectra and mass spectroscopy. Some individual grains measured *in situ* by the *Giotto* and *Vega* spacecraft did, however, show anomalous [<sup>12</sup>C]/[<sup>13</sup>C] ratios. Whereas the low (“heavy”) values might represent interference from <sup>12</sup>CH<sup>+</sup>, the high ratios (up to 5000) are similar to some values seen for micron-sized SiC grains in carbonaceous meteorites and are taken as evidence for the preservation of essentially unaltered presolar organic material (Eberhardt 1998, although there is no evidence for SiC in Halley from the high-fidelity mass spectra obtained with the PUMA-1 instrument; Schulze et al. 1997).

The three comets in which the [D]/[H] ratio has been determined are Oort Cloud comets. One could wonder what this ratio might be in Jupiter-family comets, perhaps formed at larger heliocentric distances; the answer might come from future cometary missions toward short-period comets.

#### D. The Spin Temperature of Cometary Water

As reviewed by Mumma et al. (1993), the ortho/para ratio (OPR) of cometary water is characterized by the spin temperature of this species. This parameter is believed to be of primordial character, because conversions between the ortho (hydrogen nuclear spins parallel) and para (spins opposite) states through collisions or radiative transitions are strictly forbidden. The real meaning of the spin temperature is not understood, however; it could be the temperature of water at the moment of its chemical formation, or it may reflect re-equilibration with the internal temperature of the nucleus.

The initial observations gave OPR = 2.5 ± 0.1 in 1P/Halley, corresponding to  $T_{\text{spin}} \approx 29$  K, and OPR = 3.2 ± 0.2 in C/1986 P1 (Wilson), consistent with  $T_{\text{spin}} > 50$  K (Mumma et al. 1993). However, these determinations are hampered by the difficulty in modeling opacity effects and because only part of the  $\nu_3$  vibrational band of water was observed.

ISO observed the  $\nu_3$  band of water in comets C/1995 O1 (Hale-Bopp) and 103P/Hartley 2 (Crovisier et al., 1997*b*, 1999). The full band was observed with a spectral resolution allowing resolution of the rotational structure, and the opacity was found to be moderate; see Fig. 3. Values of OPR = 2.45 ± 0.10 and 2.70 ± 0.10, corresponding to  $T_{\text{spin}} \approx 25$  and 35 K, were determined for Hale-Bopp and Hartley 2, respectively. Thus, the existence of OPR values significantly lower than the high-temperature limit of 3 is confirmed in both an Oort Cloud (Hale-Bopp) and a Jupiter-family comet. The issue is discussed further near the end of section IV.A.

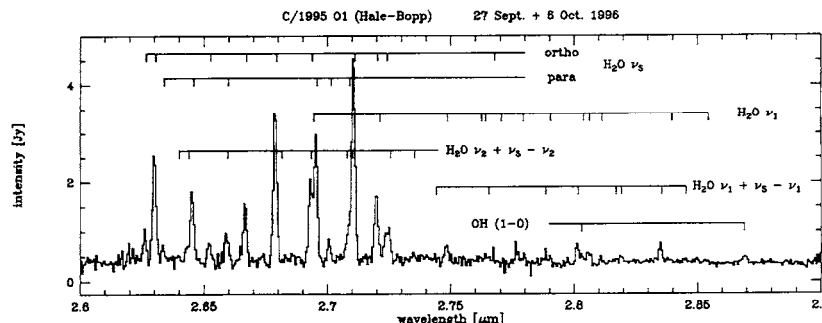
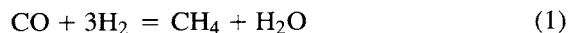


Figure 3. The region of the  $\nu_3$  band of water observed in the comet Hale-Bopp with the short-wavelength spectrometer of ISO (average of observations on September 26 and October 6, 1996, when the comet was at 2.9 AU from the Sun). The resolution of the rotation structure permits an evaluation of the rotational temperature (28 K) and of the ortho-to-para ratio ( $2.45 \pm 0.10$ , corresponding to a spin temperature  $\sim 25$  K; Crovisier et al. 1997*a,b*).

#### IV. NEBULAR CHEMISTRY OF COMETARY VOLATILES

##### A. Water

Because water is the dominant volatile in those comets for which its abundance has been determined, its origin is of prime importance for assessing how much comets represent pristine presolar material and how much presolar material reprocessed to a greater or lesser extent in the solar nebula. (We use the term “presolar” rather than “interstellar” to emphasize that some of this material may have been formed in circumstellar shells, while other portions may have been formed or modified in interstellar space.) As noted by Fegley (1993), water ice in comets could be pristine presolar ice, presolar water that was vaporized and recondensed in the solar nebula, or water synthesized in jovian protoplanetary subnebulae via thermochemical reactions such as



Even if all water in comets resulted from equation (1), which is not being advocated, this does not imply that  $\text{CH}_4$  and  $\text{H}_2\text{O}$  would be retained in a 1:1 ratio in comets, because of the greater volatility of  $\text{CH}_4$ ; the consequences of equation (1) for the  $[\text{D}]/[\text{H}]$  ratio of cometary water, and the production of intermediates such as  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$ , will be discussed below. In fact, the water in comets could be a mixture, with different comets having different proportions of pristine presolar water and reprocessed nebular water (cf. Fegley 1993; Mumma 1997).

Until *unaltered* samples of comet nuclei are accessible to chemical and physical measurements by spacecraft experiments or by laboratory

analyses of returned samples, the source of cometary water has to be inferred primarily from its hydrogen and oxygen isotopic composition. The available data are given in Tables II and III. The measured  $[D]/[H]$  ratios in Halley, Hyakutake, and Hale-Bopp cluster around  $30 \times 10^{-5}$ . This  $[D]/[H]$  ratio is about 20 times larger than the (present-day)  $[D]/[H]$  ratio in the local interstellar medium (Pisunov et al. 1997) and about twice as large as in terrestrial SMOW (Standard Mean Ocean Water), thus challenging the hypothesis that terrestrial water is derived primarily from cometary bombardments. What do the  $[D]/[H]$  ratios in Halley, Hyakutake, and Hale-Bopp tell us about the origin of water in these three comets?

One possible interpretation is that the water in these three comets is pristine interstellar water that was incorporated into the comets. The  $[D]/[H]$  ratios in cometary water are similar to the  $[D]/[H]$  ratios reported for water in the hot cores of molecular clouds, where massive stars are forming. For example, radio observations of HDO and  $H_2^{18}O$  by Jacq et al. (1990), Gensheimer et al. (1996), and Helmich et al. (1996) gave  $[D]/[H]$  ratios of order  $(20-60) \times 10^{-5}$  for hot core regions. This water vapor is thought to preserve the fractionation in the ice mantles of grains present in the cores before they were heated by the embedded young stars (Rodgers and Millar 1996). The accretion of unaltered water-bearing interstellar grains into comets may also explain the observed ortho/para ratios of cometary water vapor (discussed later in this section).

An important implication of the unmodified-interstellar-grain scenario is that other interstellar molecules will also be accreted unaltered into comets. For example, hydrogen cyanide with a  $[D]/[H]$  ratio of  $(230 \pm 40) \times 10^{-5}$  was observed in Hale-Bopp by Meier et al. (1998a), which is in the range reported in hot cores by Hatchell et al. (1998). Meier et al. (1998a) note that the  $[DCN]/[HCN]$  ratio is consistent with the  $[HDO]/[H_2O]$  ratio within the context of interstellar ion-molecule chemistry, provided that the chemistry has reached steady state and the temperature is of order 30–40 K (Millar et al. 1989). It should be noted, however, both that the interstellar hot cores are quite young, so steady-state models may not be applicable, and that the observed HCN ratio in the gas may have been diluted from an originally higher value on the presumed icy grain mantles (Hatchell et al. 1998).

Methanol ( $CH_3OH$ ) is also observed in comets (including Hale-Bopp, Hyakutake, and Halley), and it is present in hot cores, with  $[CH_3OD]/[CH_3OH]$  ratios of 0.01–0.06 (Mauersberger et al. 1988), while the  $[CH_2DOH]/[CH_3OD]$  ratio is of order unity (Jacq et al. 1993; Charnley et al. 1997). However, Eberhardt et al. (1994) reported a [deuterated  $CH_3OH$ ]/ $[CH_3OH]$  ratio  $< 0.01$  for Halley, where deuterated  $CH_3OH$  includes both  $CH_3OD$  and  $CDH_2OH$ , which could not be distinguished by the mass spectrometry. The cometary results thus seem to disagree with the deuterium fractionation for the hot cores. There are no reports of



**TABLE III**  
**[D]/[H] Ratios in Comets, the Solar System, and Interstellar Space**

Object or Species	D/H Ratio ( $\times 10^5$ )	$\delta D$ (%) <sup>a</sup>	Enrichment <sup>b</sup>	Reference
Present-day local ISM	$1.6 \pm 0.12$	-900	1	Mahaffy et al. (1998)
Solar wind	$2.1 \pm 0.5$	-865	1.3	Geiss and Gloeckler (1998)
Orion hot core: HDO/H <sub>2</sub> O	100-400	$(5.4-24.7) \times 10^3$	60-250	van Dishoeck et al. (1993)
Several hot cores: HDO/H <sub>2</sub> O	30	925	19	Gensheimer et al. (1996)
Several hot cores: DCN/HCN	90-400	$(5-25) \times 10^3$	56-250	Hatchell et al. (1998)
TMC-1: C <sub>3</sub> HD/C <sub>3</sub> H <sub>2</sub>	$(8-16) \times 10^3$	$(5-10) \times 10^6$	$(5-10) \times 10^3$	van Dishoeck et al. (1993)
TMC-1: CH <sub>2</sub> DC <sub>2</sub> H/CH <sub>3</sub> C <sub>2</sub> H	6000	385,000	3750	van Dishoeck et al. (1993)
TMC-1: DCN/HCN	2300	146,600	1440	van Dishoeck et al. (1993)
TMC-1: DC <sub>3</sub> N/HC <sub>3</sub> N	1500	95,280	940	van Dishoeck et al. (1993)
Halley: HDO/H <sub>2</sub> O	$31.6 \pm 3.4$	1030	20	Eberhardt et al. (1995)
Hyakutake: HDO/H <sub>2</sub> O	$29 \pm 10$	860	18	Bockelée-Morvan et al. (1998)
Hale-Bopp: HDO/H <sub>2</sub> O	$33 \pm 8$	1120	21	Meier et al. (1998a)
Hale-Bopp: DCN/HCN	$230 \pm 40$	13,760	144	Meier et al. (1998b)
IDPs (maximum value) <sup>c</sup>	400-800	24,800-50,000	250-500	Messenger and Walker (1997)
Venus: atm. H <sub>2</sub> O	$2200 \pm 300$	140,200	1400	Donahue (1995)
Mars: atm. H <sub>2</sub> O	$81 \pm 3$	4200	51	Donahue (1995)
Earth: SMOW	15.58	0	9.7	Lodders and Fegley (1998)
Jupiter: CH <sub>3</sub> D/CH <sub>4</sub>	$2.6 \pm 1.0$	-830	1.6	Fegley and Prinn (1988)
Jupiter: HD/H <sub>2</sub>	$2.6 \pm 0.7$	-830	1.6	Mahaffy et al. (1998)
Saturn: HD/H <sub>2</sub>	$2.5 \pm 1.0$	-840	0.9-2.2	Lodders and Fegley (1998) <sup>d</sup>
Titan: CH <sub>3</sub> D/CH <sub>4</sub>	$\sim 7.5$	$\sim -519$	$\sim 5$	Coustonis et al. (1998)
Neptune: HD/H <sub>2</sub>	$6.5 (-1.5, +2.5)$	$\sim -580$	$\sim 4$	Feuchtgruber et al. (1999)
Uranus: HD/H <sub>2</sub>	$5.5 (-1.5, +3.5)$	$\sim -650$	$\sim 3.4$	Feuchtgruber et al. (1999)
Chondrites: Semarkona (LL3)	$75 \pm 12$	$3815 \pm 170$		Delouile and Robert (1995)
phyllsilicates				
Renazzo (CR) phyllosilicates	$> 31$	$> 990$		Delouile and Robert (1995)
Chondrules (LL3, CR)	12-23	-230 to 480		Delouile and Robert (1995)
Orgueil (CI) kerogen	36.6	1360		Halbout et al. (1990)

<sup>a</sup> The delta notation is defined as  $\delta D$  (%) =  $[(D/H)_{\text{sample}}/(D/H)_{\text{SMOW}} - 1] \times 1000$  where SMOW is Standard Mean Ocean Water.

<sup>b</sup> The enrichment factor is defined as  $(D/H)_{\text{sample}}/(D/H)_{\text{ISM}}$ , taking  $(D/H)_{\text{ISM}} = (1.6 \pm 0.12) \times 10^{-5}$  as the average present day local ISM value. Measurements of the local ISM D/H ratio fall in the range of  $(1.4-2.2) \times 10^{-5}$  (Pisumkov et al. 1997).

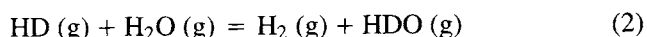
<sup>c</sup> Lower value for a particular "cluster" interplanetary dust particle, higher value for a "hotspot" on that particle.

<sup>d</sup> Griffin et al. (1996) give 2.3 (-0.8, +1.2).

deuterated  $\text{CH}_3\text{OH}$  in Hale-Bopp or Hyakutake. Finally, for formaldehyde both HDCO and  $\text{D}_2\text{CO}$  have been observed in hot cores (Sutton et al. 1995; Turner 1990; see also Rodgers and Millar 1996), whereas  $[\text{D}]/[\text{H}]$  ratios for  $\text{H}_2\text{CO}$  in comets have not been reported. Because the unmodified-interstellar-grain model implies high  $[\text{D}]/[\text{H}]$  ratios for formaldehyde in comets, it is important to see whether an upper limit for  $[\text{HDCO}]/[\text{H}_2\text{CO}]$  can be derived from the mass spectrometer data for Halley or from remote sensing observations of other  $\text{H}_2\text{CO}$ -bearing comets.

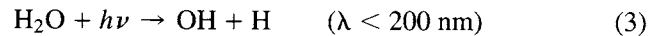
Another implication of the unmodified-interstellar-grain model is that infalling interstellar grains do not lose their volatiles during incorporation into the solar nebula. In other words, ices on infalling grains either are not vaporized or, if vaporized, do not undergo significant chemical or isotopic alteration before recondensing onto grain surfaces. In contrast, recent calculations (Chick and Cassen 1997; Cassen and Chick 1997; Engel et al. 1990; Lunine et al. 1991) indicate that a significant fraction of infalling icy grains may have been vaporized during incorporation into the solar nebula. For example, Chick and Cassen (1997) predict that the water ice vaporization distance lies between 2 and 30 AU, and Lunine et al. (1991) predict that  $\sim 90\%$  of water ice grains are vaporized at 30 AU and  $< 10\%$  of water ice grains are vaporized beyond 100 AU. While the computational results are somewhat dependent on how the solar nebula is modeled, including such poorly constrained parameters as the area/mass ratio for the infalling grains, it would seem that the vaporization of infalling icy grains may pose a hurdle for the unmodified-interstellar-grain model of cometary volatiles. These theoretical considerations and the possible lack of consistent D enrichments in cometary species such as methanol lead us to consider the alternative: that the D/H ratio of cometary water was produced either by fractionation within the solar nebula itself or by partial reprocessing of presolar water in the solar nebula.

In principle, deuterium isotopic exchange in the solar nebula between hydrogen and water (or other hydrides) via net reactions such as



leads to more HDO (or more  $\text{CH}_3\text{D}$ ,  $\text{NH}_2\text{D}$ , HDS) with decreasing temperature. Values of the D/H fractionation as a function of temperature are given for water in Fig. 11 of Prinn and Fegley (1989); comparison with the observed values in comets Hyakutake, Halley, and Hale-Bopp (Table III) indicates temperatures of order 140 K, close to the calculated water ice condensation temperatures in the solar nebula (where pressures are much higher than in the ISM). Although the correspondence with the nebular snowline is suggestive of the cometary water having been reprocessed in the solar nebula, isotope exchange kinetics at low temperatures are probably too slow for reaction (2) to have enriched water vapor in D within the lifetime of the solar nebula (Grinspoon and Lewis 1987; Fegley and Prinn 1989; Lecluse and Robert 1994).

temperatures at which the water in Hyakutake, Halley, and Hale-Bopp last exchanged deuterium with nebular H<sub>2</sub>. This could occur, for example, via reactions such as



driven by scattered solar UV and the interstellar UV radiation field in optically thin regions (e.g., the outer skin) of the solar nebula. This is essentially the reverse of the scheme proposed by Yung et al. (1988) and is also supported by recent calculations (Gladstone and Fegley 1997) that indicate that photochemistry was an important disequilibrating process in the outer solar nebula. Ion-molecule reactions driven by galactic cosmic rays in the outer skin of the solar nebula (e.g., see the suggestions of Yung et al. 1988; Deloule and Robert 1995; Aikawa et al. 1998) might also drive the back reactions, but ion-molecule chemistry may only be significant in very low-density regions of the nebula. Grain-catalyzed thermochemistry, e.g., in the subnebulae surrounding the gas giant planets during their formation, probably also played a role both by facilitating the back reaction and also by producing D-poor water [via reaction (1)] which then diluted D-rich presolar water evaporated from presolar ice grains. As discussed later, the giant protoplanetary subnebulae may also have been the sources for the CH<sub>4</sub> and NH<sub>3</sub> in comets.

In principle, the oxygen isotopic composition of cometary water can also be used to constrain its origin (Table II). The [<sup>18</sup>O]/[<sup>16</sup>O] ratio for water in Halley was measured by the *Giotto* NMS and is the same within error as the [<sup>18</sup>O]/[<sup>16</sup>O] ratio for terrestrial SMOW. More precise measurements, however, would be needed to show that water in Halley and other comets has the same oxygen isotopic composition as water on Earth. Extensive measurements of the 16–17–18 oxygen isotope ratios in meteorites by Clayton and colleagues (Clayton 1993) show that different types of meteorites have oxygen isotopic compositions that differ from each other and from the oxygen isotopic composition of the Earth-Moon system. The SNC meteorites, which are widely believed to come from Mars, and the eucrite meteorites, which are widely believed to come from 4 Vesta, also have different oxygen isotopic compositions than the Earth and Moon or than other types of meteorites. The observed differences are not due to